

Temperature compensation

This document describes the temperature compensation of measurements performed within the Unisense SensorTrace Suite software when using electrochemical sensors. The first sections describe in brief the temperature dependence of the sensors, the temperature dependence of the gas-solubilities, after which an experiment data point is compensated step-by-step.

Sensor Compensation – a-number

The electrochemical sensors have been found to obey a simple temperature dependence. The response from a sensor at constant partial pressure, but varying temperature, T , is proportional to a^T , where a is the so-called A-number.

Solubility Compensation – b-number

Henry's law states that the concentration of a dissolved gas is proportional to the vapor pressure of the gas:

$$p_{gas} = const(T, sal) \cdot [gas]$$

Here, $const$ is not really a constant but depends on temperature and salinity, making it hard to find a table value for it. Instead we rearrange the equation to $\frac{[gas]}{p_{gas}} = \frac{1}{const(T, sal)}$. This means that for data sets recorded at the same temperature and salinity, the ratio of concentration and partial pressure are the same. We use data and equations from articles¹ as a source for forming reference data. We use the subscript "table" to describe this reference data. Thus, we can write:

$$[gas] = p_{gas} \frac{[gas]_{table}}{p_{gas_{table}}}$$

Using this expression, we can convert between concentrations and partial pressures at the same temperature and salinity.

As final note, to keep the sensor temperature compensation simple, the salinity in the calculations is kept constant in the SensorTrace Suite software. If calibrating at a different salinity than measuring in, then enter the tabulated calibration concentration for the experimental salinity. E.g. when using the H₂S calibration kit.

¹ Weiss R.F. 1970. The solubility of nitrogen, oxygen and argon in water and seawater. Deep Sea Research 17:721-735
Morse J.W, Millero F.J, Cornwell J.C, & Rickard D, 1987, The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters, Earth-Science Reviews 24:1-42
Crozier T.E. & Yamamoto S. 1980. Solubility of hydrogen in water, seawater, and NaCl solutions. Journal of Chemical and Engineering Data 19:242-244
(Weiss R.F. & Price B.A. 1980. Nitrous oxide solubility in water and seawater. Marine Chemistry 8:347-359)

Concentration Compensation – step-by-step.

A user calibrates a sensor by entering matching values of mV-signal u and concentration $[O_2]$, such that, a new mV-measurement can be converted to a concentration:

$$[O_2]_{cal} = \frac{(u - offset)}{slope}$$

Using this equation neglects the temperature dependence of both the sensor and the solubility. Using the Henry's law, we can rewrite this to give the partial pressure:

$$p_{O_2,cal} = [O_2]_{cal} \cdot \frac{p_{O_2\ table,cal}}{[O_2]_{table,cal}}$$

Here the subscript "cal" indicates that the partial pressures and concentrations are measured at the temperature and salinity from the calibration. If the temperature has changed since the time of calibration, to a value T_{exp} , the sensor will have a different response to the partial pressure. However, this response is described by the a-number introduced above. At T_{exp} , the partial pressure resulting in the same signal on the sensor can be calculated from the calibration performed at T_{cal} as:

$$\begin{aligned} p_{O_2,exp} &= p_{O_2,cal} \cdot \mathbf{a}^{T_{cal}-T_{exp}} \\ &= [O_2]_{cal} \cdot \frac{p_{O_2\ table,cal}}{[O_2]_{table,cal}} \cdot \mathbf{a}^{T_{cal}-T_{exp}} \end{aligned}$$

Finally, Henry's Law can be used to convert the partial pressure at the conditions in the experiment to concentration under the same conditions.

$$[O_2]_{exp} = [O_2]_{cal} \cdot \frac{[O_2]_{table,exp}}{p_{O_2\ table,exp}} \frac{p_{O_2\ table,cal}}{[O_2]_{table,cal}} \cdot \mathbf{a}^{T_{cal}-T_{exp}}$$

This expression is used to convert a calibration (offset, slope), a signal u and two sets of experimental conditions (T_{cal}, Sal_{cal}) and (T_{exp}, Sal_{exp}) . As the salinity is considered constant at Sal_{cal} , only T_{cal} and T_{exp} are needed.

As can be seen from the equation above, the compensation consists of two factors modifying the calibration performed by the user. These two terms are also referred to as a-number (describing the temperature dependence of the sensor) compensation and b-number compensation (describing the temperature dependence of the solubility). Using these two terms the:

$$[O_2]_{exp} = [O_2]_{cal} \cdot \mathbf{b}(T_{cal}, Sal_{cal}, T_{exp}, Sal_{cal}) \cdot \mathbf{a}^{T_{cal}-T_{exp}}$$

Note, that this example uses μM as a unit. Other units measuring concentration will behave the same. Two other types of units must also be considered.

When using units of partial pressure (mbar, mmHg), $\mathbf{b} = 1$, since there is no dependence on the solubility.

For units describing partial pressure relative to saturation (% sat, % air-sat), \mathbf{b} does not depend on $[O_2]_{table,cal}$ and $[O_2]_{table,exp}$. It does, however, depend on the partial pressure at saturation which changes with temperature.